

# Pattern formation and self-organization in precipitation systems, design and control of patterns in the micro and nanoscales

## Final Research Report

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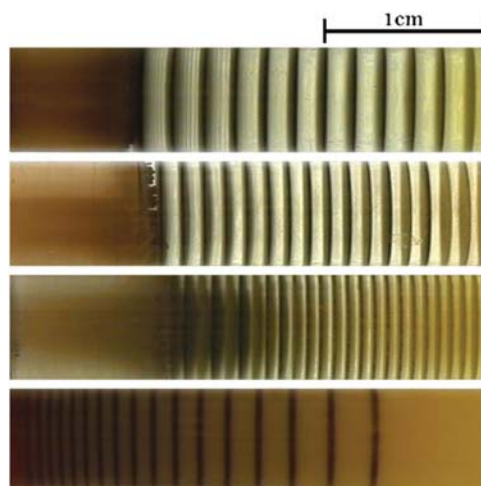
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During this project the important aspects of the pattern formation in precipitation systems were investigated. Spontaneous pattern formation can be observed at all length scales and much effort has been devoted to gaining insight into the dynamics of these processes. One of the aims of these studies is to reproduce and control the emerging patterns, thereby opening possibilities for applications such as, e.g., the downsizing of electronic devices. For practical purposes, reaction-diffusion processes which yield bulk precipitation patterns are especially important since they are building blocks for the so-called *bottom-up* or *bulk* approach to structure design (to be contrasted with *top-down* methods where material is removed to create structures, as in case of lithography). The use of precipitation processes, however, is limited due to problems over their control. Indeed, precipitation can be influenced by appropriately chosen geometry, by boundary conditions, or by a combined tuning of the initial and boundary conditions, but all the above methods are unwieldy, and developing more flexible approaches would be clearly valuable.

**1. Pattern control using an electric field** (I. Bena, M. Droz, I. Lagzi, K. Martens, Z. Rácz and A. Volford, *Designed patterns: flexible control of precipitation through electric currents*, *Phys. Rev. Lett.*, 101, 075701, 2008)

We introduced a general and easily realizable tool of control based on employing pre-designed electric currents for regulating the dynamics of the reaction zones in the system. The method originates in two observations. First, precipitation patterns are often formed in the wake of moving reaction fronts whose reaction dynamics specifies where and when precipitation thresholds are crossed. Hence control over precipitation should be realized through controlling the reaction front. Second, the reacting species are usually oppositely charged ions. Hence the details of the control: an appropriately directed electric field or current strongly affects the concentration of reagents in the reaction zone and, consequently, it can be used to govern the crossing of precipitation thresholds and thus the location of the precipitate. Different equidistant patterns can be designed based on this idea (Figure 1).



**Figure 1** Experimentally designed precipitation patterns. Lowest panel illustrates the usual Liesegang bands.

Our results on the control of precipitation patterns have important theoretical as well as practical implications. From a theoretical point of view, they demonstrate the predictive power and, implicitly, the correctness of our phase separation in the presence of a moving source scenario for Liesegang pattern formation. Indeed, these are the first experiments which test intricate details of the theory and the agreement is excellent.

**2. Pattern control varying the precipitation threshold (solubility product)** (F. Molnár jr., F. Izsák and I. Lagzi, *Design of equidistant and revert type precipitation patterns in reaction-diffusion systems*, *Phys. Chem. Chem. Phys.*, 10, 2368-2373, 2008)

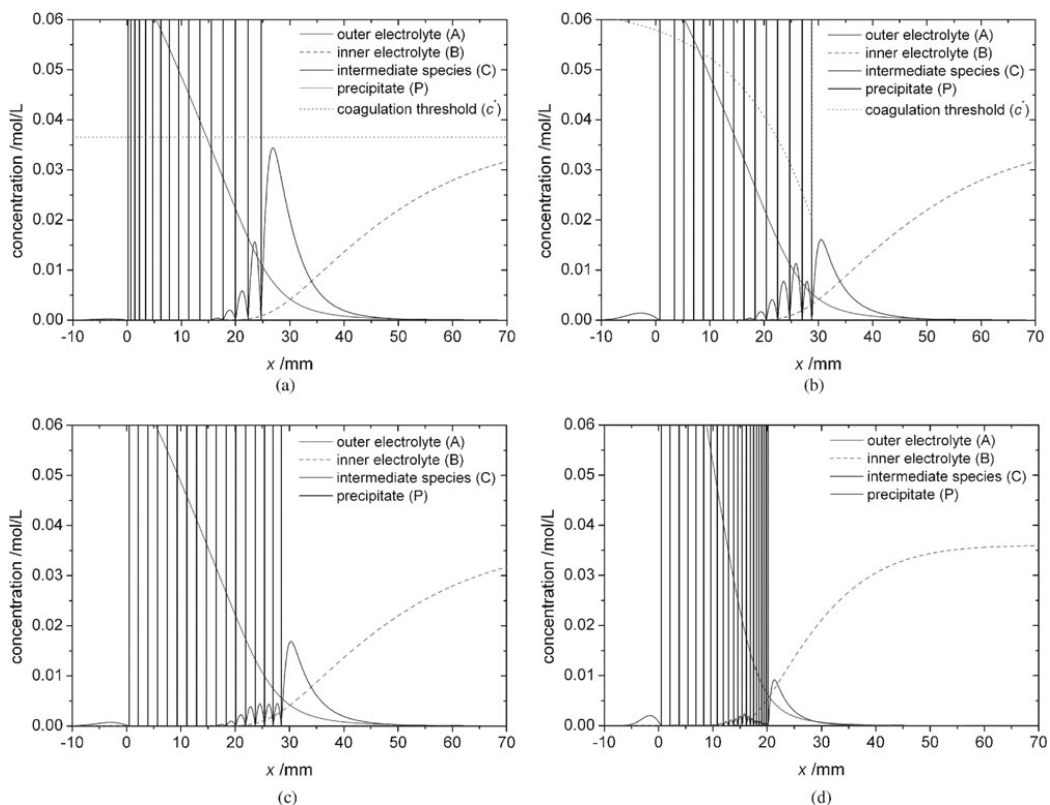
We also provided a simple and general method to modify and control the precipitation pattern in reaction–diffusion systems varying the precipitation threshold (solubility product). Using this technique different type of patterns can be generated (converging, diverging, and even equidistant, Figure 2). The main advantage of the method is that arbitrary patterns can be generated in a diffusion system without any external forces as advection or ionic migration. Equidistant pattern can be formed only in a case when the coagulation threshold coincides with the corresponding value of the coagulation limit function. Taking smaller threshold values in every position at any time results in inverse type (converging) pattern, while higher ones result in Liesegang like (diverging) precipitation structures. The precipitation threshold cannot be directly changed; it can be coupled other parameters, e.g. temperature and light intensity.

We provided a simple explanation to understand the mechanism of revert pattern formation (Figure 3). A relevant interpretation of revert or irregular precipitation pattern structures in nature could be explained by the fact that in these systems this governing precipitation threshold may vary spatially and/or temporally. In nature there is no indication that this limit should be constant compared to experiments in thermostatic conditions. This threshold itself may depend on the chemical and physical properties of the system. Therefore classical regular patterns cannot be expected in all cases. From the technological point of view, the most important is how design and control microscopic or even nanosize patterns on material surfaces or in porous media. One should prepare

surfaces and porous media by prescribed methods in a way that it indirectly controls the precipitation threshold.

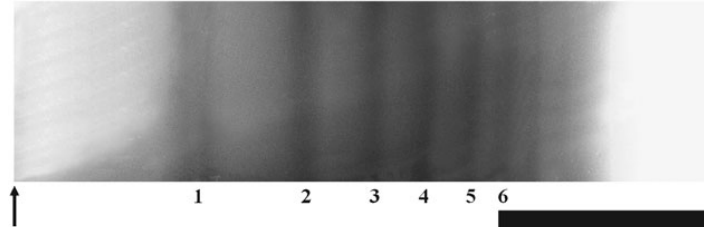
**3. Pattern control and transition** (I. Lagzi and D. Ueyama, *Pattern transition between periodic Liesegang pattern and crystal growth regime in reaction-diffusion systems*, *Chem. Phys. Lett.*, 468, 188-192, 2009)

Precipitation pattern formation in different gels and pattern transition in mixed agarose–gelatin gel were investigated. Different type of pattern structures can be designed using chemically different gels (Figure 4), and pattern transition from Liesegang pattern to crystal growth can be controlled by addition of gelatin to agarose gel (Figure 5). Based on our investigations it is implied that the Liesegang pattern formation (periodic precipitation) is not a robust phenomena, and such type of pattern formation can be expected only in systems, where the diffusion matrix (hydrogel, aerogel, liquid, etc.) provides high heterogeneous (or homogeneous) nucleation rate and number density of particles. Furthermore, this rate should not be too high because at very high rate the diffusion cannot deplete the inner electrolyte from the vicinity of bands due to continuous nucleation and precipitate formation. This means that Liesegang pattern formation occurs only in a moderate nucleation regime, lower and higher rates favor to macroscopic crystal growth and continuous precipitation in reaction–diffusion systems.

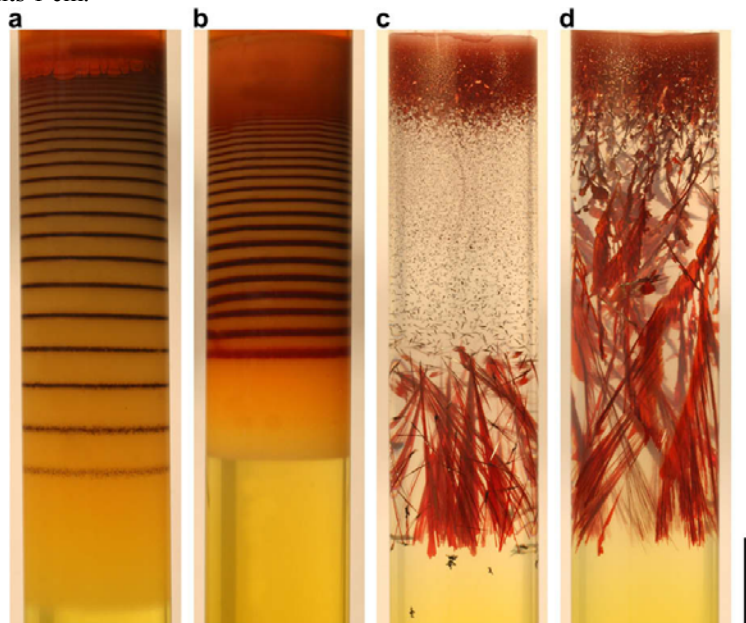


**Figure 2** Spatial distribution of the intermediate species, precipitate and the outer and inner electrolytes respectively at  $t = 168.00$  h. Images show the following cases: (a) diverging Liesegang-like pattern where the coagulation threshold is a function of time, decreasing slower than prescribed for an equidistant pattern; (b) equidistant pattern with 1.6 mm wavelength, created by a spatially inhomogeneous coagulation

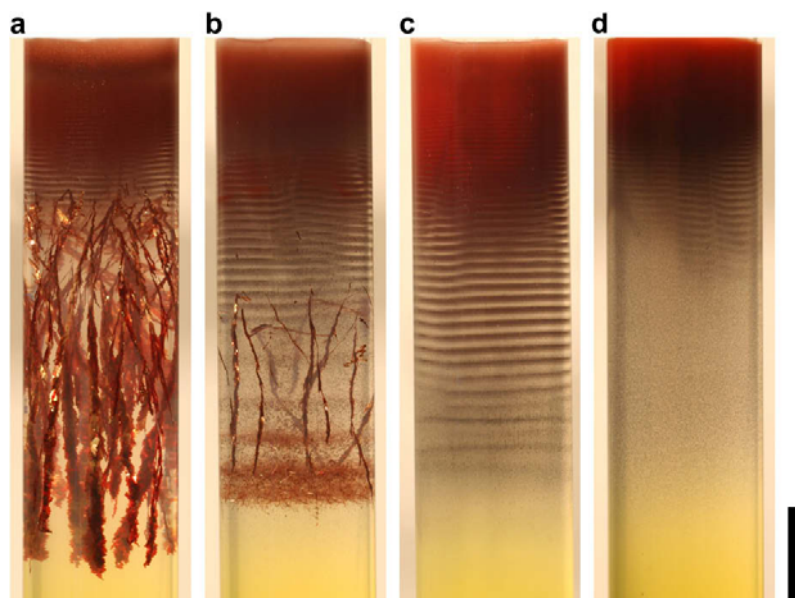
threshold ; (c) equidistant pattern with 1.6 mm wavelength, created by a time-dependent coagulation threshold; (d) revert-type pattern where the coagulation threshold is a function of time, decreasing faster than prescribed for an equidistant pattern.



**Figure 3** The revert (inverse) AgI precipitation pattern in gelatin gel (16%) after 3 weeks. The distance between two consecutive bands is decreasing, which is in contrast to the regular Liesegang phenomenon, where it must be increasing. The concentration of the outer ( $\text{AgNO}_3$ ) and inner (KI) electrolytes were 0.4 and 0.04 M, respectively. The arrow indicates the junction point of the outer and inner electrolytes. The scale bar represents 1 cm.



**Figure 4** The silver dichromate precipitation patterns after 1 week at  $20.2 \text{ }^\circ\text{C} \pm 0.4 \text{ }^\circ\text{C}$  in gelatin gels: (a) 5 w/w%, (b) 10 w/w% and in agarose gels: (c) 0.25 w/w% and (d) 0.5 w/w%. The concentrations of the inner (potassium dichromate) and the outer (silver nitrate) electrolytes are 0.0036 M and 0.25 M, respectively. The scale bar represents 1 cm.



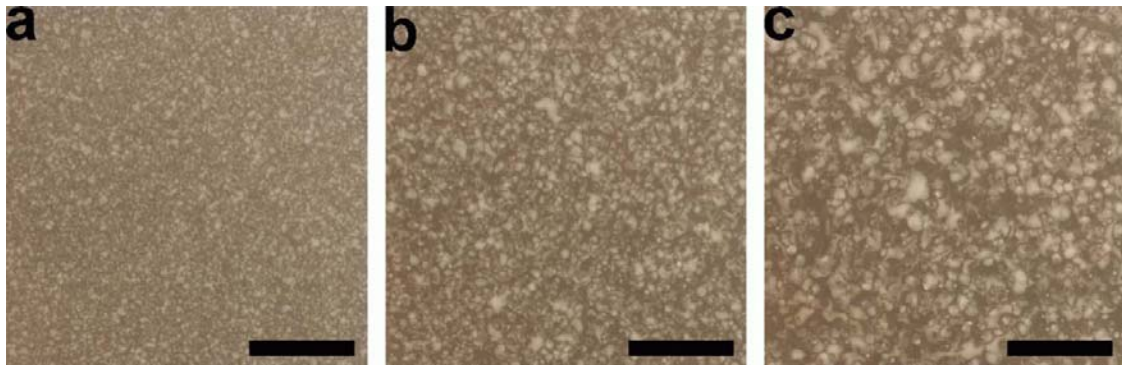
**Figure 5** Pattern transition from crystal growth to periodic precipitation after 1 week at  $20.2 \text{ }^\circ\text{C} \pm 0.4 \text{ }^\circ\text{C}$  in mixed agarose–gelatin gels: (a) 0.5 w/w%/0.001 w/w% (b) 0.5 w/w%/0.005 w/w% (c) 0.5 w/w%/0.01 w/w% and (d) 0.5 w/w%/0.1 w/w% (gelatin/agarose concentration). The concentrations of the inner (potassium dichromate) and the outer (silver nitrate) electrolytes are 0.0036 M and 0.25 M, respectively. The scale bar represents 1 cm.

One can see that very small amount of gelatin can induce pattern transition in reaction–diffusion systems. There are several important effects that influence pattern formation, namely rates of heterogeneous and surface nucleation (nucleation on crystal surface) and variation of supersaturation. In such systems, there is practically no homogeneous nucleation because the gel matrix has internal structure which provide nucleation sites (and also may contain impurities) so the dominant nucleation process is the heterogeneous nucleation. This internal structure (pore size etc.) depends on the gel type, its chemical grade and as well as the gel concentration. The gelatin provides higher nucleation rate and number density of crystal than agarose. In case of higher nucleation rate there is no surface nucleation, which favors to formation of periodic precipitation (Liesegang phenomenon). Inside the Liesegang bands the number of crystals is very high, but the size of crystals is small (1–10  $\mu\text{m}$ ). In contrast to this fact, the agarose ensures lower nucleation rate, the number density of crystal is also lower compared to gelatin. Therefore, in this case the initial dominance of heterogeneous nucleation will be exceeded by the nucleation on crystal surface and the growth of crystal aggregates reduce the supersaturation at a high enough to suppress further heterogeneous nucleation. These result in growth of macroscopic needle- and plate-like crystal aggregates. This is a simple interpretation why the patterns have different morphologies in different gels. It can be controlled by gel quality, gel concentration and quality and concentration of reacting species. The pattern transition can be explained in a similar manner. Small amount of gelatin can induce heterogeneous nucleation and the number density of crystals is high because of higher supersaturation at the interface. This involves the occurrence of periodic precipitation near to the junction point of the electrolytes. The higher the distance from the interface is, the lower the supersaturation becomes, resulting in a continuous decrease in the number of density of crystals. Small crystals can grow and the

surface nucleation will be preferred producing needle- and plate-like crystal aggregates after periodic precipitation zone. Increasing the gelatin concentration in the mixed gel, the heterogeneous nucleation rate and the number density of crystals will be so high in the diffusion medium that only periodic precipitation will be dominant (or some needle- and plate-like aggregates can be observed). However, at higher gelatin concentration continuous precipitation can be observed after the periodic precipitation region due to high nucleation rate

**4. Coarsening of precipitation patterns in a moving reaction-diffusion front** (A. Volford, I. Lagzi, F. Molnár jr., Z. Rácz, *Coarsening of precipitation patterns in a moving reaction-diffusion front*, *Phys. Rev. E*, 80, 055102(R), 2009)

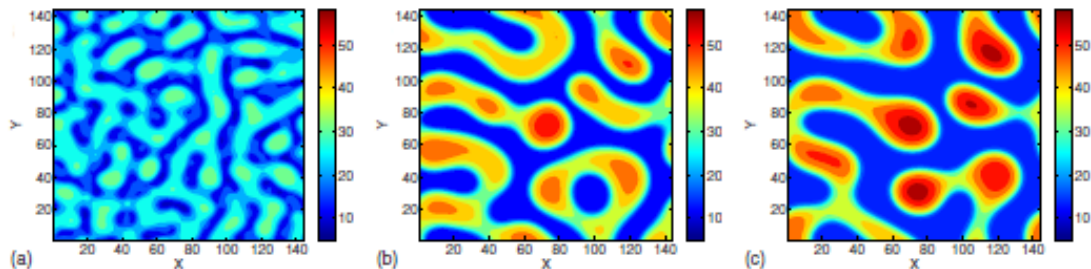
Our aim was to initiate experimental and theoretical studies of the coarsening dynamics of the transverse patterns in reaction zones. This task is made feasible experimentally by overcoming the transparency problem in a way suggested by earlier studies of Liesegang-type phenomena. Namely, the reaction-diffusion process is set in a nearly transparent gel and, furthermore, appropriately chosen electrolytes are used so that the reaction product undergoes redissolution in the excess of the outer electrolyte. As a result, precipitate exists only in a narrow region restricted to the reaction zone and its time evolution can be followed in detail. We observed the patterns in a moving reaction zone in  $\text{Al}(\text{OH})_3$  precipitation system (Figure 6).



**Figure 6** Time evolution of the precipitation pattern in the reaction zone for the samples with  $[\text{NaOH}] = 2.5$  M (outer electrolyte) and  $[\text{AlCl}_3] = 0.52$  M (inner electrolyte). The front moves perpendicularly to the plane of the picture and the pictures were taken at  $t_1 = 180$  s (a),  $t_2 = 480$  s (b), and  $t_3 = 960$  s (c) after the initiation of the reaction. The length of the scale bars is 1 cm.

The experimental observations suggested that the system displayed a self-similar coarsening and this was quantified through the time dependence of the characteristic length scale  $\xi(t)$  of the pattern, with the main experimental result being that  $\xi(t) \sim t^{1/2}$ . Theoretically, the effective dimensionality of the coarsening system is not entirely obvious, and there are several candidates for driving the coarsening process. We studied this problem by generalizing the Cahn-Hilliard theory (Figure 7) of precipitation to include sources and sinks coming from the emergence of the reaction product in the reaction zone and from the redissolution of the precipitate in the excess outer electrolyte, respectively. The numerical solutions of the equations in three dimensions are in agreement with the experimentally observed  $\xi(t) \sim t^{1/2}$ . This suggests the natural picture

that the sources and sinks are relevant perturbations on the particle conservation, and we observe a curvature-driven late-stage coarsening in a model with nonconserved order parameter.



**Figure 7** Simulation results using Cahn-Hilliard phase separation model.

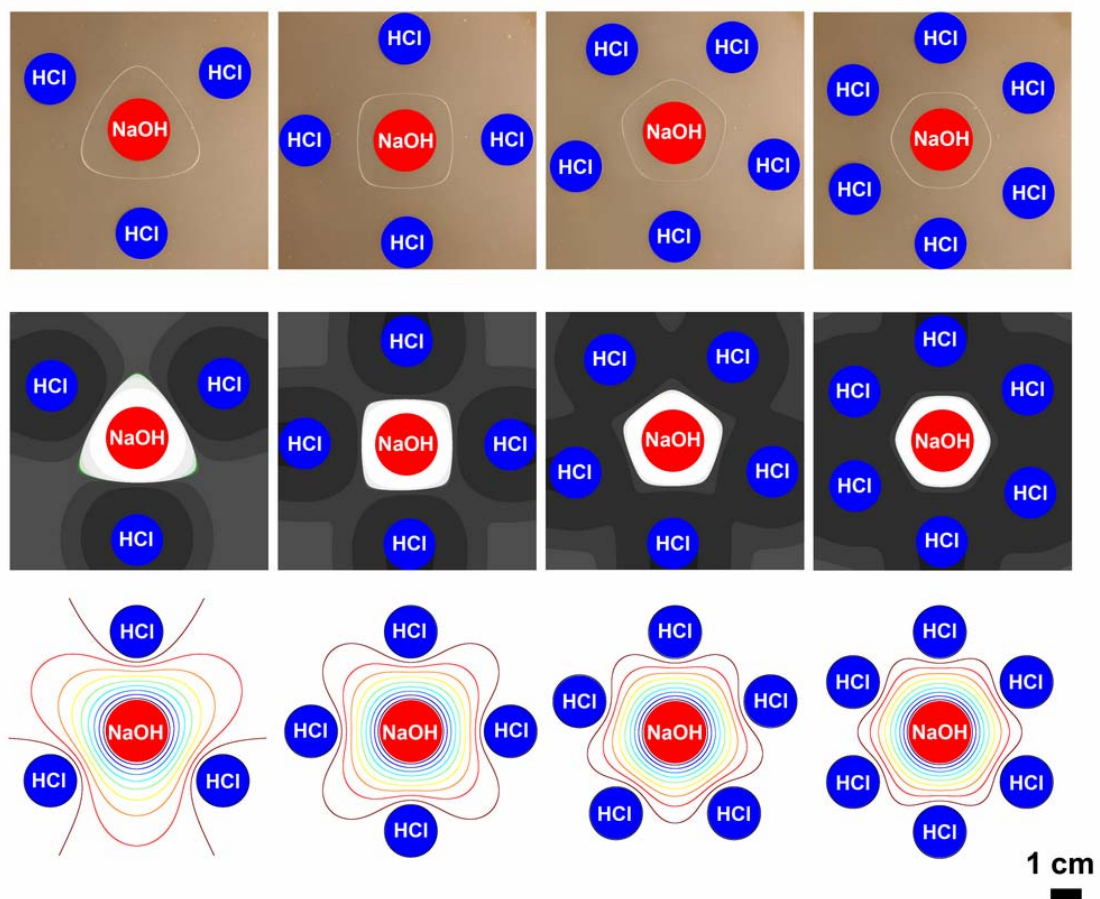
**5. Numerical modeling using video cards with CUDA** (F. Molnár jr., T. Szakály, R. Mészáros and I. Lagzi, *Air pollution modelling using a Graphics Processing Unit with CUDA*, *Comput. Phys. Commun.*, 181, 105-112, 2010)

Modeling of scientific problems mostly requires solution of the reaction-diffusion equations (partial differential equations, PDE). Numerical solution of these equations in three dimensions is one of the most challenging applied mathematical problems. These simulations are very time consuming, therefore, ideas and strategies that can reduce the calculation time are important topics of research. A general and robust idea is the parallelization of source codes/programs. Recently, the technological development of graphics hardware created a possibility to use desktop video cards to solve numerically intensive problems. In the past years, the technological development of consumer graphics hardware created the possibility to use desktop video cards to solve numerically intensive problems in various fields of science (chemistry and physics, astronomy, medical sciences, geosciences, environmental sciences and mathematics), since their computational capacity far exceeds that of the desktop processors. The main advantage of using (processors of video cards) for general purpose calculations is its high cost-effectiveness compared to supercomputers, clusters or GRID systems. Programming GPUs for general computation was a great challenge in the past, but NVIDIA has created a parallel computing architecture called Compute Unified Device Architecture, or CUDA, which simplifies the programming significantly providing documentations and required programming applications.

There have only been a few trials in the literature to solve various types of PDEs using CUDA environment. We presented efficient techniques to utilize GPU computing power using CUDA to solve an air pollution related problem. Our group at the Eötvös Loránd University was the first among these research communities, who showed and presented several applications (simulation of dispersion of air pollutants and simulation of reaction-diffusion problems) using GPU computing with CUDA. This paper published in *Computer Physics Communications* is in a list of the **TOP 25 Hottest Article** (<http://top25.sciencedirect.com/subject/computer-science/7/journal/computer-physics-communications/00104655/archive/26/>).

**6. Controlling precipitation patterns by pH field** (F. Molnár, L. Roszol, A. Volford and I. Lagzi, *Control of precipitation patterns in two-dimensions by pH field*, *Chem. Phys. Lett.*, 503, 231-234, 2011)

Knowledge on pattern control and distortion of structures in a bulk phase are among of the important raising questions in material science. We provided a simple way to distort and control of the evolution of the precipitation structure resulting in stationary profiles in 2D (Figure 8). Numerical approaches, solving either time dependent reaction-diffusion equations or solving derived Laplace's equation, provide a reasonable description of the system. Moreover, our results indicate that in some systems, where the precipitation occurs by reaction of hydroxide ions, the system is governed by a complex pH field and the pattern formation can be described and discussed by a simple way taking only acid-base chemistry into account. This strategy can be extended to design and control complex structure by acid-base chemistry in 3D.



**Figure 8.** Stationary front profiles using different arrangements of the peripheral acidic reservoirs: experiments at  $t = 5$  h (top row); numerical simulation results of reaction-diffusion equations at  $t = 5$  h (Eqs. 1-2, middle row); numerical simulation results of Laplace's equation (Eq. 3, bottom row). In numerical simulations the colors correspond to the different concentration levels of  $H^+$ .